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AN ALLOY FOR THERMAL SPRAYING
[Yousha yoo gookin]

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Specification

1. Title of the invention

An alloy for thermal spraying

2. Scope of patent claims

1. An alloy for thermal spraying that is characterized by the fact that it is composed of the addition of 1 – 7% of Al and 0.2 – 2% of Si to a 12 – 30 Cr-Fe alloy.

2. An alloy for thermal spraying that is characterized by the fact that it is composed of the addition of 1 – 7% of Al, 0.1 – 2% of Si (preferably 0.2 – 2%), and 0.001 – 0.1% of B to a 12 – 30 Cr-Fe alloy.

3. Detailed description of the invention

The present invention relates to an alloy for thermal spraying that is optimal for use in thermal spraying onto the surface of a component to be used under thermolytic conditions, such as in a gas turbine combustion cylinder or a heating furnace for petroleum refining.

In general, in terms of the properties that are desirable in said components, in addition to thermal resistance at high temperatures, the components should have

oxidation resistance as well as corrosion resistance in relation to sulfur or vanadium.

Conventionally, for said components, it is common to use Fe-Cr steel, Cr-Ni-Fe steel, or Mo, but none of these materials show sufficient high temperature corrosion resistance, and in particular, there is insufficient corrosion resistance in relation to vanadium, so these materials were limited in use up to maximum temperatures of 800°C - 900°C.

Also, with the recent development of spraying methods for powder alloys or ceramics, materials with superior corrosion resistance are now used in powder form to perform thermal spraying, but from the standpoint of spraying efficiency, it is best to use the spray material as a round bar in order to perform the spraying.

The present invention enables thermal spraying in a round bar shape, and even in comparison to other methods, it can provide an alloy for thermal spraying that has superior corrosion resistance up to higher temperatures, and that has favorable adhesion properties with other metals.

In other words, the present invention provides an alloy for thermal spraying that has superior high temperature corrosion resistance, in which it is not only

possible to easily form a round bar through the addition of a specific amount of Al and Si to an Fe-Cr alloy, but it is also possible to improve the adhesion properties between the spray layer and other metals. Further, the present invention aims to further improve the adhesion properties and corrosion resistance by the further addition of a specific amount of B to said alloy.

In general, Fe-Cr alloys have corrosion resistance. However, when considering the processing properties of

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these alloys, when the Cr amount is within the range of 12 – 30%, it is possible to simultaneously satisfy both the corrosion resistance properties and the processing properties. Therefore, as a result of various experiments with a variety of additives to a basic composition of a 12 – 30 Cr-Fe alloy for use as an alloy for thermal spraying, the following was learned.

First, by adding a certain amount of Al to a 12 – 30 Cr-Fe alloy, the coating will have exceedingly superior oxidation resistance at high temperatures. This efficacy will become effective when adding 1% or more of Al, but when adding 7% or more, there will be a reduction in the processing properties of the alloy, so it is preferable for the addition range of the Al to be 1 – 7%. Further, even

when applying the Fe-Cr-Al alloy with the above composition range to thermal spraying, it is possible to form a spray coating, resulting in a coating that has corrosion resistance properties and oxidation resistance properties. However, because the adhesion properties between this coating and another metal are not necessarily satisfactory, and because there is a tendency to see an increase in the pore ratio when forming a coating layer, the coating may become dislodged at high temperatures, and as a result, the material will be insufficient for use as a coating.

In order to resolve these problems, and to obtain a better alloy for thermal spraying, in which the adhesion properties have been improved and the pore ratio has been reduced, it is preferable to further add a specific amount of Si or B to said alloy.

In other words, during the spraying operation, the Si will improve the fluidity of the molten material that is attached as a coating layer, so it is possible to reduce the presence of pores that could be formed due to the presence of the Al. In order to obtain this efficacy, the addition amount of Si should be 0.2% or more. If the addition amount of Si exceeds 2%, there will be a reduction in the processing properties of the material, which is undesirable.

Further, a similar efficacy can be seen when adding B as is seen when adding Si, and said fluidity can be achieved by adding a minute (0.001% or more) amount of B. Therefore, this can act to maximize the reduction in the pore ratio of the coating layer, and it can also further improve the corrosion resistance of the coating. When the addition amount of B exceeds 0.1%, the processing properties of the material will be exceedingly poor, which is undesirable.

Next, Table 1 shows the results of an experiment to look at the properties of the spray coating that was obtained using a linear bar composed of the alloy composition according to the present invention. Table 1 shows the compositions of the linear bars that were used, and the properties of the resultant spray coating, such as the adhesion properties (the degree of adhesion between the coating and another metal), the pore ratio, and the corrosion resistance. For comparison, data from the case of a linear bar of 18 Cr-0.1 Si-Fe is also shown.

Table 1

Material number	Composition (weight %)					Properties of the spray coating		
	Cr	Al	Si	B	Fe	Adhesion properties	Pore ratio	Corrosion resistance
1	15.2	5.3	0.05	-	Bal	Normal	Large	Good
2	20.6	5.5	0.2	-	Bal	Somewhat good	Small	Good
3	19.6	3.1	0.6	-	Bal	Good	Small	Good
4	18.9	5.5	0.15	0.001	Bal	Good	Medium	Very good
5	24.2	3.3	0.5	0.004	Bal	Good	Small	Very good
6	24.8	5.5	0.15	0.003	Bal	Good	Small	Very good
7	25.9	6.8	0.15	-	Bal	Normal	Large	Good
8	28.1	2.9	0.1	-	Bal	Normal	Large	Good
9	18.5	-	0.1	-	Bal	Normal	Small	Poor

The following is clear from the results in Table 1. In other words, based on the cases of material numbers 2, 3, 5, and 6, it is clear that Si can play a large role in a reduction in the pore ratio. Further, in order to sufficiently achieve this efficacy, it is preferable to add 0.2% or more, and as shown in material numbers 1, 2, 7, and 8, when the Si addition amount is 0.2% or less, there will be little reduction in the pore ratio.

Also, when adding B, it is clear from material numbers 4, 5, and 6 that there will be a significant reduction in the pore ratio even at small amounts Si, but as shown in material number 5, it is preferable to use an Si amount of 0.2% or more in order to achieve a synergistic effect. It is important to note that, in terms of this B addition efficacy, there will be a marked improvement in the

corrosion resistance of the coating, irrespective of the presence of Si.

Therefore, the alloy according to the present invention that can be obtained by adding specific amounts of Al and Si, and if desired, B, to a Fe-12-30 Cr alloy can be processed as a round bar for thermal spraying, and further, it is possible to obtain a coating that will have superior corrosion resistance (in particular, there will be sufficient corrosion resistance in relation to S and V) and

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oxidation resistance when formed as a coating, with good adhesion properties to other metals and with a small pore ratio.

Further, the coating that can be obtained using this alloy will sufficiently show said properties even at high temperatures such as 1200°C, so from the standpoint of the fact that the usage limit for other conventional corrosion resistant coating was a maximum temperature of 900°C, it is clear that this is a coating with exceedingly superior corrosion resistance.

Figure 1 and Figure 2 show the corrosion resistance properties and oxidation resistance properties when forming a 0.1 mm spray coating on top of a stainless steel plate

using material number 3 and material number 6 as noted in Table 1.

In other words, in terms of the corrosion resistance, corrosion processing was performed by immersing said sprayed plate within combustion ash (80% V_2O_3, 20% Na_2SO_4) that was heated and melted at 900°C, then cathodic treatment was performed on the plate within a salt bath at 550°C (60% NaOH, 40% Na_2CO_3). The scales that were generated as a result of corrosion were removed, and measurements were made of the corrosion weight loss by treatment hour. Figure 1 shows the results of these measurements. In Figure 1, curve 1 represents the results from the corrosion testing on material number 3, and curve 2 represents the results from the corrosion testing on material number 6. Also, for comparison, the same corrosion processing was performed on a 18Cr-8Ni stainless steel plate and a 25Cr-20Ni stainless steel plate as are commonly used in the internal lids of conventional heating furnaces, and the corrosion weight loss was measured for these materials, where these results are also shown in Figure 1.

Also, for the oxidation resistance properties, measurements were made of the oxidation weight loss for each heating hour when heating the plate that was coated in the same manner as above to a temperature of 1100°C. In

Figure 2, curve 1 is the case of material number 3, and curve 2 is the case of material number 6. Also, for comparison, Figure 2 shows the case of a 25Ni-20Cr stainless steel plate.

As is clear from Figures 1 and 2, the coating that was obtained when using the alloy for thermal spraying according to the present invention showed superior corrosion resistance and oxidation resistance.

Therefore, when using the alloy for thermal spraying according to the present invention as a coating for a heat resistant component such as in a gas turbine combustion cylinder or in a heating furnace for petroleum refining, there will be a major improvement in the operation efficiency of the apparatus.

It is also acceptable to add an additive such as Ti, Zr, Ce, or Y, which is known to result in effective activity for corrosion resistance and oxidation resistance when used in conventional alloys, to the alloy for thermal spraying according to the present invention either alone or as a complex within an addition range of 1% or less, because even as a result of this addition, there will be no reduction in the efficacy of the present invention, and it will be possible to further improve the corrosion resistance and oxidation resistance.

4. Brief explanation of the drawings

Figure 1 is a diagram showing the relationship between the processing time and the corrosion weight loss of the coating formed using the alloy for thermal spraying according to the present invention, together with the comparative examples. Figure 2 is a diagram showing a similar relationship for the oxidation weight loss.

Figure 2

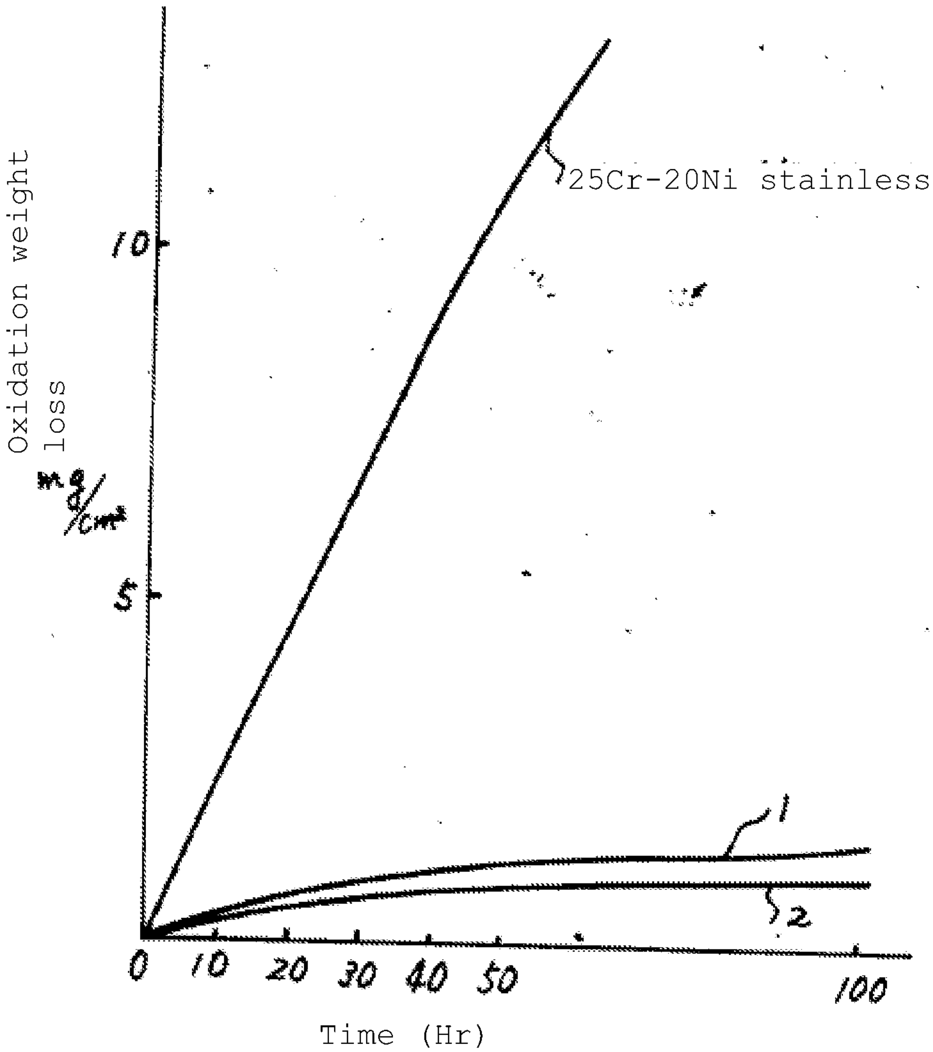
25Cr-20Ni stainless
Oxidation weight loss
mg/cm²
10
5
1
2
0
10
20
30
40
50
100
Time (Hr)

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Figure 1

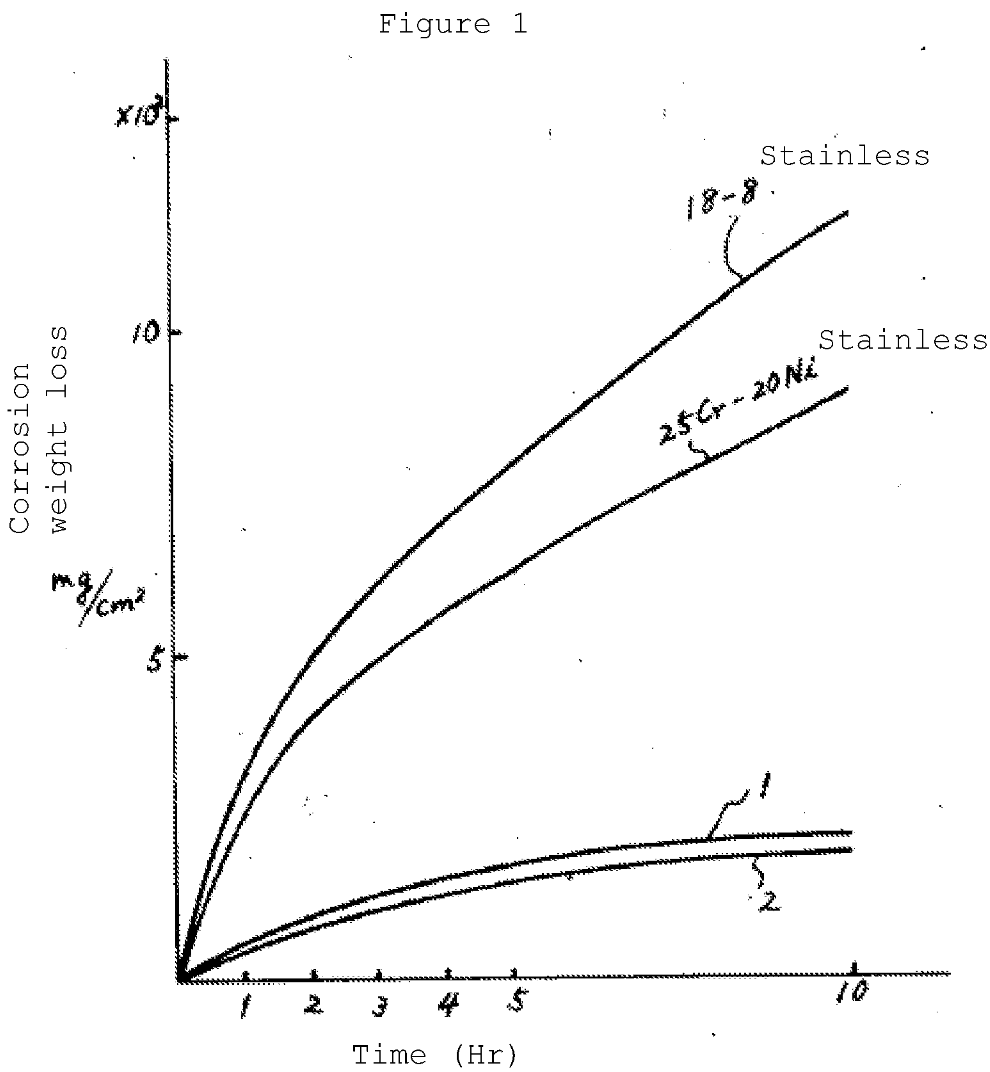

Figure 1
x10³
10
5
Corrosion weight loss
mg/cm²
Stainless
18-8
Stainless
25Cr-20Ni
1
2
1
2
3
4
5
10
Time (Hr)